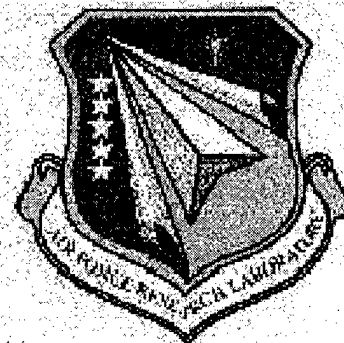


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**DEVELOPMENT OF CATALYST FOR SELECTIVE
REDUCTION OF NO_x AND OXIDATION OF CO AND
HYDROCARBONS**

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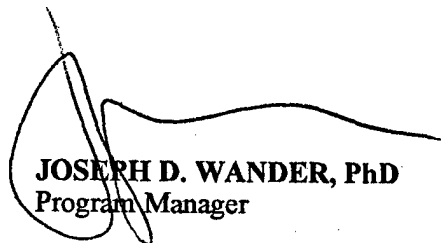
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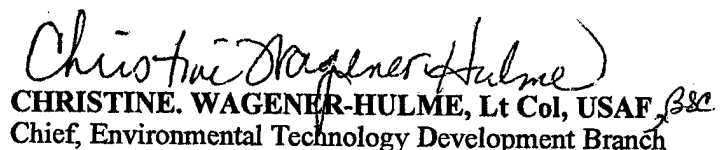
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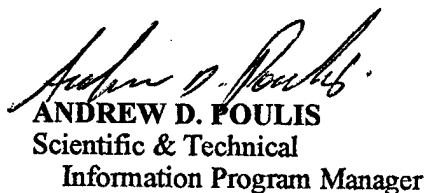
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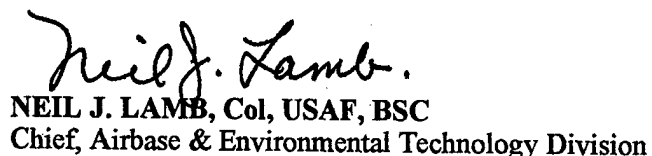
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PREFACE

This SBIR Phase I final technical report was prepared by Energy & Environmental Research Corporation, 18 Mason, Irvine, CA 92618. This report documents work conducted under a Small Business Innovation Research award, contract F08635-91-C 0174 between 25 April 1997 and 25 October 1997. Dr. Joseph Wander was the technical monitors for the project, Department of the Air Force, Air Force Research Laboratory, Airbase and Environmental Technology Division (AFRLIMLQE), 139 Barnes Drive, Suite 2, Tyndall AFB FL 32403-5323.

This report describes the laboratory scale testing of two possible methods of catalytically reducing NO_x in diesel exhaust. Of the two NO_x control methods tested one was found to unpromising while the other gave promising results when propane was used as the NO_x reducing agent.

EXECUTIVE SUMMARY

DOD's plan to make all U.S. military equipment run on a single fuel, logistics fuel, has obvious logistics advantages, but will require replacement of spark ignition engines with diesel engines or gas turbines. Both diesel engines and gas turbines are systems which must be operated fuel lean. Consequently the three-way catalyst system used in automobiles can not be used to control their emissions and a different method of pollution control must be sought.

While there are a number of satisfactory alternatives for control of CO and unburned hydrocarbons, no satisfactory method of NO_x control is available. Research is currently underway to develop ion-exchanged zeolites as NO_x control catalysts but catalysts of this type suffer from a number of problems. They are unstable and deactivate under the conditions of high temperature and high partial pressure of steam encountered in practical use.

While this problem of catalyst stability has been receiving considerable attention, another, more subtle, problem has been largely ignored. In the numerous published studies light hydrocarbons such as propane were used as the NO_x reductant. While the mechanism by which this reduction occurs, there is a substantial evidence that it involves an initial gas-phase oxidation of some of the hydrocarbon which converts the NO to NO₂. The catalyst then adsorbs the NO₂ and it is somehow reduced to N₂. While the latter stages of this mechanism are poorly defined, the gas phase process is well understood, at least in broad outline. The slow gas phase oxidation of hydrocarbons produces HO₂ free radicals and other free radicals. Just which other free radicals one gets depends on the hydrocarbon. The HO₂ free radical converts the NO into NO₂ via the well known rapid reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$. If the other radicals do not react with the NO₂ to convert it back into NO, the NO can be efficiently converted to NO₂. If, however, they do, the conversion will not be efficient and consequently the hydrocarbon will not provide an efficient reduction of NO to N₂.

Thus one can reasonably worry that a catalyst which has been shown to work in a satisfactory manner with light hydrocarbons might be unsatisfactory with logistics fuel.

In this research two types of NO_x reduction systems were tested. Since both these systems were mixtures of materials with good stability at high temperature and steam partial pressure they were, potentially, an improvement on the zeolites in terms of durability. For both systems there

were theoretical reasons to expect/hope that the reduction would occur via a mechanism which would work equally well irrespective of the reductant used.

For one of these systems, i.e., the silver-based catalyst, this hope proved false. The data indicate that NO reduction occurred via the same NO-to-NO₂-to-N₂ mechanism as with the zeolites. While apparently very promising results were obtained for this catalyst with propane as the reductant, the results with diesel fuel were clearly unfavorable.

For the second system, a mixture of a sorbent and an oxidation catalyst, the results may be described as a qualitative success and quantitative failure, i.e., as is discussed below in detail, this system did everything one would want but not well enough to be potentially useful. While some of these failures might be overcome with further research, it seems very likely that systems of this kind will always be too bulky and heavy for satisfactory use on mobile and/or portable equipment.

Accordingly EER will not be proposing a Phase II program.

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1. INTRODUCTION

1.1 OBJECTIVE

The objective of this project was to do a laboratory scale proof of concept experiment demonstrating the selective catalytic reduction of NO_x by hydrocarbons in simulated diesel exhaust.

1.2 BACKGROUND

1.2.1 DEFINITION OF THE PROBLEM

NO_x Control for Systems Fueled with Logistics Fuel The spark ignition engine is unique among combustion devices in that it is capable of satisfactory operation with fuel/air mixtures which range from fuel rich to fuel lean. While automobiles powered by spark ignition engines can emit unacceptable amounts of NO_x , CO and unburned hydrocarbons, they also can be tuned to operate at almost exactly stoichiometric conditions. This allows emissions to be very effectively controlled with the "three way catalyst" system now in general use in the U.S., Western Europe, and Japan.

DOD's plan to make all U.S. military equipment run on a single fuel, logistics fuel, has obvious logistical advantages, but will require replacement of spark ignition engines with diesel engines or gas turbines. Both diesel engines and gas turbines are systems which must be operated fuel lean. Consequently the three-way catalyst system can not be used to control their emissions and a different method of pollution control must be sought.

1.2.2 CURRENTLY AVAILABLE NO_x CONTROL TECHNOLOGIES

NO_x Control via Combustion Modification and via Post Combustion Exhaust Treatment

There are two approaches to controlling the emission of air pollutants by combustion systems: modifying the combustion process so that the exhaust does not contain pollutants and post combustion removal of the pollutants. The former has been quite successful as a method of controlling the NO_x emissions of coal-fired power plants and many other stationary combustion systems. Suitable adjustment of the combustion process also allows limiting the CO and unburned hydrocarbon emissions of diesel engines and gas turbines to very low levels. Controlling NO_x emissions to acceptably low levels is, however, more difficult for gas turbines and very difficult for diesel engines. Thus to control the NO_x emissions of diesel engines and gas turbines it is necessary to use some type of post combustion NO_x reduction.

Nonselective Reduction of NO_x Many catalysts for reducing NO_x have been reported in the literature. Thus, for example, Lindstedt, Stromberg, and Milh¹ have reported a group of perovskite catalysts of the formula La_{1-x}Sr_xMO₃ (M = Fe, Co), which allow nearly quantitative reduction of NO by CO in the temperature range 600°C to 950°C Provided oxygen is absent. In the presence of oxygen NO is not reduced unless the amount of CO used was sufficient for complete reduction of both the oxygen and NO present.

Diesel and gas turbine exhaust contains very large amounts of O₂, typically 5 to 15 percent, while the NO_x is generally less than 600 ppm. Reducing the NO_x along with such a large amount of O₂ would require using prohibitively large amounts of the reducing agent. Thus the NO_x reduction process needs to be selective, reducing all (or nearly all) of the NO_x while leaving the O₂ largely untouched.

Selectively Reducing NO_x: Reduction with NH₃ Two such selective reduction technologies have been developed and successfully commercialized. In one (the SCR process) a catalyst is used to promote the selective reduction of NO_x by ammonia. In the other technology (the Thermal DeNO_x process²) use of a reaction temperature in the range of 700°C to 1000°C allows the selective reduction of NO_x by ammonia without the need for any catalyst. Ammonia precursors such as urea can also be used in the same temperature range.

Both the Thermal DeNO_x process and the SCR process have been highly successful for controlling NO_x emissions in situations in which it was feasible to supply the needed ammonia. From a military viewpoint, however, the need to supply ammonia would appear to be a substantial disadvantage, violating the logistics fuel concept.

1.2.3 EMERGING NO_x CONTROL TECHNOLOGIES

Selectively Reducing NO_x: Reduction with Hydrocarbons If an NO_x reduction technology is to be compatible with the logistics fuel concept, the reducing agent it uses has to be logistics fuel. While there are no commercially developed technologies for selective NO_x reduction which do not use ammonia, numerous authors have reported laboratory experiments in which light hydrocarbons were used for the selective catalytic reduction of NO_x.

Unfortunately, however, in some of the early studies the NO_x was initially present as NO and the analytical methods used would not distinguish between the reduction of NO to N₂ and the oxidation of NO to NO₂. As is well known the low temperature oxidation of hydrocarbons produces the HO₂ free radical and HO₂ reacts rapidly with NO, converting it to NO₂. Thus in

some early reports conversion of NO to NO₂ was mistakenly regarded as removal of the NO_x, making the reported removal higher than it was in fact.

Despite this confusion there have been other studies which unambiguously show the existence of a family of catalysts (zeolites which have been ion-exchanged with copper, iron, platinum, cobalt, gallium, cerium and hydrogen ions)³ are indeed capable of selectively reducing NO_x with hydrocarbons as the reducing agents. The mechanism of this reduction appears to involve the initial oxidation of the NO to NO₂ which is then captured by the catalyst and reduced to N₂.

While catalysts of this kind might be used to control NO_x from military diesel engines and gas turbines, there are three important difficulties involved in such an approach. Firstly zeolite based catalysts are unstable at high temperatures in the presence of water vapor. Thus, although catalysts of this kind have shown promising initial activity, they tend to lose activity at an unacceptably high rate.

Secondly small amounts of sulfur poisons these catalysts. Since the U.S. Air Force must buy locally available fuel throughout the world, a severe restriction on the fuels sulfur content would be an awkward constraint.

Thirdly there is a more subtle problem which has been largely ignored. The slow, gas-phase oxidation of hydrocarbons produces HO₂ free radicals and other free radicals. Just which other free radicals form depends on the hydrocarbon. The HO₂ free radical converts the NO to NO₂ via the well known, rapid reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$. If the other radicals do not react with the NO₂ to convert it back into NO, the NO can be efficiently converted to NO₂. If, however, they do, the net conversion into NO₂ will not be efficient and consequently the hydrocarbon will not provide an efficient reduction of NO to N₂. Thus it is quite possible that logistic fuel will not reduce NO_x with this kind of catalyst or do so poorly even though such catalysts are successful with light hydrocarbons.

Selective Adsorption of NO_x The technical literature also includes a number of proposed NO_x control technologies in which a sorbent is used to selectively remove NO_x from exhaust or flue gas by selective adsorption. (See, for example, the recent paper by Eguchi et. al.⁴ and references cited therein.) While a number of sorbents are known which will rapidly and selectively remove NO_x from exhaust and flue gas, there is the problem that the sorbent becomes saturated and must be regenerated, i.e. after removing NO_x from the flue gas by passing it through the sorbent, one must pass a second gas stream through the sorbent and desorb the NO_x into it. For this transfer

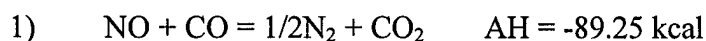
of NO_x from one gas stream to another to be practically useful the concentration of NO_x in the second gas stream must be considerably higher than it was in the flue gas. This means that the desorption step must be done at a higher temperature than was the sorption step.

Raising the temperature of a packed bed of sorbent is, however, an awkward process. The outer layers of the bed tend to insulate the interior of the bed, making heat transfer a slow and difficult procedure.

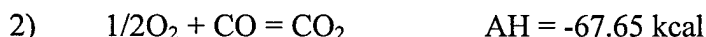
In principle a packed bed of sorbent can be heated internally by doing combustion within the bed. In practice, however, this is generally not a feasible approach since combustion tends to be an all or nothing process: at locations in the bed at which the fuel and air mixture do not ignite, no heat is generated, while wherever ignition does occur far too much heat is liberated, and the local temperature increases excessively with destructive results.

1.2.4 THE APPROACH TO NO_x CONTROL FOLLOWED IN THIS RESEARCH

Silver on Alumina: The Concept of an Electrochemical Approach Often, when a problem seems to be insoluble, the difficulty is that one has been thinking about it in the wrong terms. In the usual formulation the reduction of NO by CO would be written as

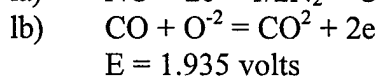
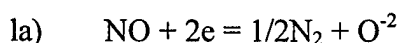


The competing reduction of O_2 is written as



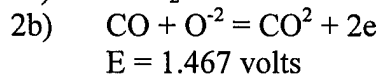
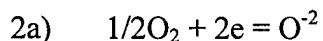
In this formulation the problem is that a catalyst is needed which allows the first but not the second reaction to occur rapidly but both reactions are strongly exothermic.

If, however, one thinks of these reactions in electrochemical terms, the first reaction becomes pair of half cell reactions:



$$E = 1.935 \text{ volts}$$

The second reaction becomes



$$E = 1.467 \text{ volts}$$

Subtracting one finds that the voltage of the 1a half cell reaction is 0.468 volts greater than the

2a half cell reaction. With such a large voltage difference it should be quite possible to selectively reduce NO electrochemically without reducing O₂.

Figures 1A and 1B show calculations for this approach for reaction temperatures of 500°C and 1000°C. As these figures show, for reaction temperatures from 500°C to 1000°C the redox reaction of Ag/Ag₂O with NO is thermodynamically favorable but the reaction with O₂ is unfavorable and cannot occur. Thus, assuming that there is little or no overvoltage for the Ag → AgO reaction, Ag/Ag₂O will selectively reduce NO.

It is, of course, a large assumption. It requires that the reaction mechanism be electrochemical. While this is a real possibility, there are a number of other possibilities. Furthermore assuming no overvoltage for the Ag → AgO reaction implies that the overall reaction rate is limited by the overvoltage for the reduction of the AgO.

While these are questions which can be resolved only by experiment, this approach does have some advantageous features. Silver catalysts, especially silver supported on high surface area alumina are used commercially for a number of petrochemical processes. Since in these processes they are exposed to water vapor at high temperatures, their stability would not appear to be an issue.

Since silver sulfide reacts rapidly in an oxidizing atmosphere to form silver oxide and SO₂, poisoning by sulfur would not appear to be an issue.

Finally, if the electrochemical mechanism discussed above is correct, the selective reduction of NO_x will work equally well for all carbon monoxide, light hydrocarbons and the heavier hydrocarbons in diesel fuel.

Unmixed Combustion in the presence of an NO_x Sorbent

The second approach to controlling NO_x emissions used in this research is based on a new concept developed by Energy and Environmental Research called Unmixed Combustion. In this new concept fuel and air are alternately passed through a packed bed containing a readily oxidized metal/readily reduced metal oxide, e.g. Ni/NiO supported on high surface area alumina. The air oxidizes the metal to the oxide while becoming depleted of oxygen and the fuel reduces the oxide back to the metal while being oxidized to CO₂ and water vapor. Thus combustion occurs without the necessity of mixing fuel and air.

One of the potential advantages of unmixed combustion relates to the heating of packed beds. The unmixed combustion catalyst can be distributed throughout the bed. Since the amount of heat liberated by combustion in any section of the bed will be proportional to the amount of

unmixed combustion catalyst in that section of the bed, unmixed combustion can serve as a highly effective method of uniformly heating a packed bed.

Thus unmixed combustion might be a satisfactory method of regenerating packed beds of an NO_x sorbent. Suppose, for example, a packed bed consisting of a mixture of an NO adsorbent and a Ni/NiO unmixed combustion catalyst is used. Exhaust gas at some temperature T is passed through the bed. Provided this temperature is low enough, the sorbent removes NO from the exhaust gas. As the bed nears saturation with NO, a pulse of hydrocarbon fuel is put through the bed. The reduction of NiO to Ni by hydrocarbons is a weakly endothermic process. Thus, for example, the reaction $10\text{NiO} + \text{C}_3\text{H}_8 = \text{Ni} + 3\text{CO}_2 + 4\text{H}_2\text{O}$ is endothermic by 8.44 Kcal per mole of NiO. Consequently the temperature of the bed decreases slightly during the reduction step and the adsorbed NO_x remains on the sorbent.

As soon, however, as the hydrocarbon pulse is over, the oxygen in the exhaust gas starts oxidizing the Ni back to NiO. This strongly exothermic process occurs first at the end of the packed bed nearest the exhaust gas inlet and moves through the bed toward the outlet. The increase in the bed temperature causes the sorbent to release the NO into the gas phase. The released NO_x is swept downstream through regions of the bed in which the Ni has not yet been oxidized to NiO. It is well known that Ni reacts rapidly with both O_2 and NO. Consequently it is to be expected that most of the released NO will be reduced to N_2 .

Thus it would appear possible to use a combination of a selective adsorbent and a nonselective reduction to achieve the selective reduction of NO in the presence of large amounts of oxygen. Such an approach might be particularly interesting for military applications, since it would be expected to work equally well with any fuel.

1.3 SCOPE

This report describes research done under a DOD Phase I SBIR program awarded under Contract No. F41624-97-C0009, "Development of a Catalyst for Selective Reduction of NO_x and Oxidation of CO and Hydrocarbons". The Introduction of this report discusses the nature of the problem of NO_x emissions from military diesel engines and explains why presently available or proposed NO_x control technologies are poorly suited to this application. Two new, and possibly more suitable, approaches to controlling NO_x emissions from diesel engines are described.

The experimental methods used in this research are summarized in Section 2. Section 3 summarizes the experimental results of this study and of previous related studies done by EER. Section 4 examines the scientific and engineering implications of these results.

Section 5 reports the conclusion of this examination and makes recommendations. Of the two NO_x control methods tested one was found unpromising while the other gave promising results when propane was used as the NO_x reducing agent. Since, however, the results with diesel fuel as the reducing agent were not promising, further development did not seem justified. Instead it is recommended that the need to use diesel fuel as the NO_x reductant in any practical control method for NO_x from diesel engines be carefully considered in future research planning.

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS/CATALYST PREPARATION

Silver Based Catalysts In these studies two silver based catalysts were used. one of these catalysts was prepared by purchasing a 10 wt% silver nitrate on +50 mesh alumina and calcining it to produce a material that was 6.8 wt% silver on +50 mesh alumina.

The second silver catalyst was prepared by the incipient wetness method, i.e., a 51 wt% solution of silver nitrate in water was prepared and added to Norton alumina rings slowly with constant stirring until the alumina rings could not absorb any more solution without appearing wet. The preparation was then calcined to produce a 37.9 wt% silver on an alumina catalyst support.

Ni/NiO Unmixed Combustion Catalyst 400 grams of Norton alumina rings and 495 grams of nickel (II) nitrate hexahydrate were placed in a pan on a hot plate and stirred while the nickel (II) nitrate hexahydrate melted and was absorbed by the alumina rings. On calcination and reduction this produced a catalyst containing 27.3 wt% Ni.

Cu/CuO Unmixed Combustion Catalyst 327 grams of Norton alumina rings and 288 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ were placed in a pan on a hot plate, a small amount of water was added and the mixture stirred while the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was absorbed by the alumina rings. on calcination and reduction this produced a catalyst containing 21.4 wt% Cu.

Sorbent 19 wt% Cr_2O_3 on alumina pellets was purchased from Johnson Matthey Corporation.

Preparation of Catalyst/Sorbent Mixtures In some of the experiments reported below mixtures of an unmixed combustion catalyst with a NO_x sorbent were used. Since the catalyst was supported on 8mm OD alumina rings while the sorbent was supported on 4mm-diameter alumina cylinders, there was a considerable difference in size and bulk density. A mixture of the two showed a strong tendency to self separate with the lighter rings rising to the top. To assure that the packed beds used in these experiments were reasonably homogeneous the charges of catalyst and sorbents were divided into 10 equal portions. A first portion of the sorbent and a first portion of the catalyst were taken and alternately added in small increments to the reactor. This procedure was repeated with the remaining 9 portions of sorbent and catalyst.

Gases and Reagents 99.9 percent pure nitrogen was purchased from Air Products Corporation

as was a certified mixture of 3030 ± 5.5 ppm of NO in nitrogen. Propane was obtained from Matheson Corporation. The n-pentane used was technical grade from EM Science Corp. Diesel fuel was purchased from an Exxon station.

2.2 EXPERIMENTAL SETUPS

The experimental setup used for testing the silver based catalysts with either a steady flow of hydrocarbon reductant or with the hydrocarbon reductant added in pulses is shown in Figure 2.

Figure 3 shows the setup used for testing the mixture of Ni/NiO catalyst and Cr_2O_3 on alumina sorbent. In this setup liquid hydrocarbon reductants were injected via syringe needle.

The setup used for testing the mixture of Ag/ Ag_2O catalyst and Cr_2O_3 on alumina sorbent and the mixture of Cu/CuO catalyst and Cr_2O_3 on alumina sorbent is also shown in Figure 3. In this setup liquid hydrocarbon reductants were also used, again injected via syringe needle. A precision metering pump was used to transfer water from a reservoir to a heated length of stainless steel tubing in which it boiled and was added to the flowing gas mixture. A flow of CO_2 was also added, the amount added being regulated via a needle valve and adjusted to give a 5.0% reading on the CO_2 meter.

The analytical train in all three setups included a Thermoelectron Chemiluminescent NO_x meter, a Fuji Electric IR CO/CH_4 analyzer and a Fuji Electric IR CO_2 meter.

3. RESULTS

3.1 RESULTS FROM PREVIOUS EER STUDIES

Design Concept for the Cr_2O_3 System In a previous study¹ EER examined the possibility of controlling NO_x emissions from an engine by using a pressure-swing selective sorbent. The design concept, shown in Figure 4, was that the exhaust from the engine would be cooled by passage through a fin cooler, and then be passed alternately through either of two beds of sorbent to remove the NO_x it contained. While the exhaust was being purified by passage through one of the beds, the absorbed NO_x in the other sorbent bed would be removed by a vacuum pump and returned to the engine.

While sending the NO_x back to the engine would cause some increase in the amount of NO_x coming out of the engine, much of the recycled NO_x would be consumed in the combustion process. Thus it was entirely possible to recycle the NO_x to extinction.

Test Results The experimental setup shown in Figure 5 was used to examine the removal of NO_x by a bed of 19 wt% Cr_2O_3 on alumina by pressure-cycled selective absorption. The results, presented in Table 1, show the sorbent provided >90% removal of NO_x for operating temperatures from 165°F to 633°F. The system was used for more than 1000 cycles without any noticeable loss of performance.

3.2 SILVER CATALYSTS WITH STEADY FLOW OF PROPANE

Figure 6 shows the results of an experiment done with the setup shown in Figure 1 in which the 6.8-wt% silver catalyst was used to reduced NO with C_3H_8 as the hydrocarbon reductant. Experiments were also done with CO but as long as the amount of oxygen present was sufficient for complete CO oxidation, no NO_x reduction was observed. During these experiments the pressure drop through the reactor was observed to be excessive due to the catalyst's small particle size (+50 mesh).

Figure 7 shows the results of an experiment also done with the setup shown in Figure 1 setup in which the 37.9 wt% Ag catalyst on alumina rings was used to reduced NO. During these experiments the pressure drop through the reactor was found to be negligible.

3.3 SILVER CATALYSTS WITH PULSED FLOW OF PROPANE

Figure 10 shows the results of an experiment done with the setup shown in Figure 3 in which pulses of C_3H_8 were injected into the reactor at 10 minute intervals, the C_3H_8 input rate corresponding to a time averaged input of 0.11% of the total flow.

3.4 SILVER CATALYSTS WITH DIESEL FUEL

The setup in Figure 2 was modified so that the propane reductant was replaced with diesel fuel. The amount of diesel fuel used was determined by passing the experimental mixture through the oxidation catalyst and measuring the amount of CO_2 produced (1.5 volume percent of the total flow). This experiment produced the results shown in Figure 9.

3.5 SILVER, COPPER, AND NICKEL CATALYSTS IN MIXTURE WITH Cr_2O_3 SORBENT

In the experiments done with the mixture of the Ni/NiO unmixed combustion catalyst and Cr_2O_3 sorbent both $n-C_5H_{12}$ and diesel fuel were used as hydrocarbon reductants. It was found that both fuels were oxidized by NiO only at temperatures so high that the Cr_2O_3 sorbent would not capture NO_x .

In the experiments done with the mixture of the Ag/ Ag_2O unmixed combustion catalyst and Cr_2O_3 , sorbent, however, it was found that the Ag/ Ag_2O unmixed combustion catalyst readily oxidized diesel fuel at $600^\circ F$, a temperature low enough for the Cr_2O_3 sorbent to efficiently capture NO_x . Steady flows of the gas mixture through the catalyst/sorbent mixture were maintained at 2000v/v/hr while recording the NO_x concentration in the gases exiting the reactor.

To remove the NO_x which the Cr_2O_3 sorbent captured, one cc of diesel fuel was injected at intervals of one hour. Injection of the diesel fuel immediately caused the CO_2 meter to go offscale showing that the fuel was rapidly oxidized. This oxidation would be expected to suddenly raise the bed temperature and cause absorbed NO_x to be released. Consistent with this expectation the NO_x output spiked, i.e. the NO_x output showed a peak with an average height of 4280 ± 70 ppm and a width at half height of 10 seconds. Following the spike the NO_x output rapidly dropped to 100 ± 4 ppm then slowly rose to 172 ± 2 ppm by the end of the hour. With each subsequent injection of diesel fuel this process repeated itself.

Thus in these experiments the initial removal of NO_x was 57.5 percent but the NO_x emitted subsequently amounts to 3.9 percent so that the net removal was 53.6 percent.

If, instead of injecting one cc diesel fuel, 1.5 milliliters was used, the fraction of the input NO_x which is initially captured rises to 63.6%, the size of the NO_x output spike drops to 1.4%, and the net removal is 62.2%.

Experiments similar to the above were done with a 23/77 mixture of 21.4-wt% copper on alumina catalyst and the 19-wt% Cr_2O_3 -on alumina sorbent. While the results of these experiments were qualitatively similar to the above, in quantitative terms they were less favorable, the initial capture averaging only 36 percent of input and the amount NO emitted in the spike being 9.1 percent.

4 DISCUSSION

4.1 CRITERIA FOR A SATISFACTORY NO_x CONTROL TECHNOLOGY

In comparing the results reported above with other approaches to controlling NO_x emissions from diesel engines, the extent of NO_x reduction achieved is only one of several factors of importance. For example, in both these experiments and many of the NO_x -control technologies proposed in the literature, a hydrocarbon reductant is used to reduce NO_x to nitrogen and water. Clearly the amount of hydrocarbon used needs to be acceptably small. Specifically it needs to be both small enough not to be an unacceptably loss of fuel economy and it needs to be small enough that the heat from oxidizing the hydrocarbon can be disposed of without severe engineering problems. While the definition of "unacceptable" will vary from one application to another, in most instances it will probably be necessary to limit fuel consumption by the catalyst to a value below 3 to 5 percent of engine fuel consumption.

Secondly, to avoid logistics problems, the hydrocarbon used to reduce the NO_x needs to be the same as the hydrocarbon used to fuel the engine. Thus it has to be diesel fuel.

Thirdly the catalyst must be durable both under its normal operating conditions and whatever more extreme conditions it is likely to encounter.

Finally the weight and volume of the catalyst necessary for effective NO_x control must be acceptably small. For systems to be installed on trucks and other vehicles this requirement means that catalyst operation at $\geq 100,000$ v/v/hr is desirable. For other system in which space and weight are less of a constraint this requirement will be lower.

4.2 EVALUATION OF SYSTEMS TESTED

Direct Selective Reduction of NO with Silver Catalysts Compared to the ion-exchanged zeolites proposed in the literature as NO_x control catalysts, the silver-on-alumina catalyst had an

advantage in that its components are materials stable at high temperature and steam partial pressures. Thus it might prove stable at conditions the zeolite systems might not survive.

It also appears possible that, with further development the 100,000 v/v/hr target might be achieved.

In terms of the fuel economy requirement discussed above, the results obtained with propane for this system seem, at first glance, to be promising. In Figure 8 a 67 percent NO_x reduction occurs with a hydrocarbon input of 0.47 mole-percent propane while in Figure 9 only 0.17 mole-percent propane produced NO_x reductions as high as 43 percent. These mole-percent propane inputs correspond to 2.6 percent and 0.94 percent of fuel consumption, respectively.

Unfortunately diesel fuel is the practically important case and here the results are far less favorable. While Figure 11 shows up to 42 percent NO_x reduction, achieving this reduction required a diesel fuel input corresponding to 22 percent of engine fuel consumption. It does not seem likely that such a large loss in fuel economy would be acceptable.

The electrochemical mechanism discussed above predicts that the silver-based catalyst would be effective for No reduction and that CO and propane and diesel fuel would be equally effective reductants with such catalysts. While the results do show that a silver-based catalyst can indeed provide effective NO reduction, it appears that this reduction does not occur via an electrochemical mechanism.

The mechanism frequently proposed for reduction of NO by hydrocarbons on ion-exchanged zeolites involves a gas-phase oxidation of the hydrocarbon which converts the NO to NO₂, the NO₂ then being captured by the zeolite and there reduced. If this mechanism is also operative for the reduction of No on silver, one would expect the effectiveness of the catalyst -to vary with the reductant used and for CO to be totally ineffective. This is consistent with, but obviously not proven by the results.

Reduction of NO by Selective Absorption and Nonselective Reduction. In the experiments with the Cr₂O₃ sorbent and the silver and platinum catalysts, durability is likely since all the components of this mixture are known from the literature to be stable at relatively high temperatures and steam partial pressures. The one cc of diesel fuel used in these experiments corresponds to 4.3 percent of engine fuel consumption.

The space velocity, however, was only 2000 v/v/hr. This low space velocity is typical of what is necessary in sorbent systems because of the time necessary for the gas passing through the bed to

approach equilibrium with the interior of the sorbent particles.

5 CONCLUSIONS AND RECOMMENDATIONS

The goal of this research, finding a catalyst suitable for reducing the NO_x in diesel engine exhaust, has also been the goal of many other research projects. The size of this research effort can be judged from the fact that during the past year the journal Applied Catalysis, Environmental, has published 22 papers on this topic. These papers from research groups scattered throughout the world are probably only the "tip of the Iceberg", since research on catalysis is often kept proprietary or published in other journals. For all of these 22 papers and for all research projects of which EER is aware, the NO_x reductant studied was a chemically pure light hydrocarbon.

This similarity between all these different research projects is worrisome because it means that they can all fail for the same reason: the catalyst developed may work perfectly with one or another chemically pure light hydrocarbon and still be practically useless with diesel fuel. It does not seem likely that either of the NO_x control systems tested in this project could be developed into a system suitable for DOD needs. All these systems being developed by others appear to rely on essentially the same chemistry as the silver catalyst tested in this research. Thus there is a real worry that, like silver, they will not work well with hydrocarbons in the diesel/logistics fuel range.

EER's recommendation is that this worry be faced on all future research planning.

6 REFERENCES

- 1 A. Lindstedt, D. Stromberg, and M. A. Milh, Applied Catalysis A--General 116, 109-126 (1994)
- 2 R. K. Lyon. Reducing the Nitric oxide Content of Combustion Effluents, U.S. Patent 3,900,559.
- 3 For references see M. D. Amiridis et. al. "Selective Catalytic Reduction of Nitric Oxide by Hydrocarbons, a Review", Applied Catalysis B: Environmental 10, 203-227 (1996)
- 4 K. Eguchi, M. Watabe, S. Ogata, and H. Aria, Journal of Catalysis 158, 420-426 (1996)
- 5 R. K. Lyon "Pipeline Compressor Engine NO_x Control", Phase I Final Report, Contract No 5089-254-1847, Copies available from author upon request

TABLE 1

SUMMARY OF RESULTS OF THE SORBENT LIFETIME TEST

Cycle	Bed Temperature	[H ₂ O]	NO Removal
1 - 360	165 ^o F	1%	>99% throughout cycle
360 - 422	165 ^o F	4.7%	>99% throughout cycle
422 - 452	165 ^o F	4.7%	Slowly declining from 99% to 98% removal.
452 - 482	165 ^o F	4.7%	At the start of this interval NO removal
482 - 644	165 ^o F	4.7%	During this interval NO removal at the start and end of the cycle declined to 97% and 58% respectively.
644 - 790	284 ^o F	4.7%	Immediately following the increase in sorbent bed temperature the NO removal became negative, i.e. the gas coming out of the bed contained more NO than that going in. With time this evolution of NO from the bed declined. By 790 cycles the initial No capture was 93%.
790 - 879	410 ^o F	4.7%	Again increasing the bed temperature causes a brief period of negative NO capture. As this transient decays, NO capture improves, reaching 99% by cycle 879.

Cycle	Bed Temperature	[H2O]	NO Removal
879 - 937	520°F	4.7%	Again increasing the bed temperature causes a brief period of negative NO capture. As this transient decays, NO capture improves, reaching 96% by cycle 937.
954 - 959 between 88 and 97%	633°F	4.7%	No equilibrium capture

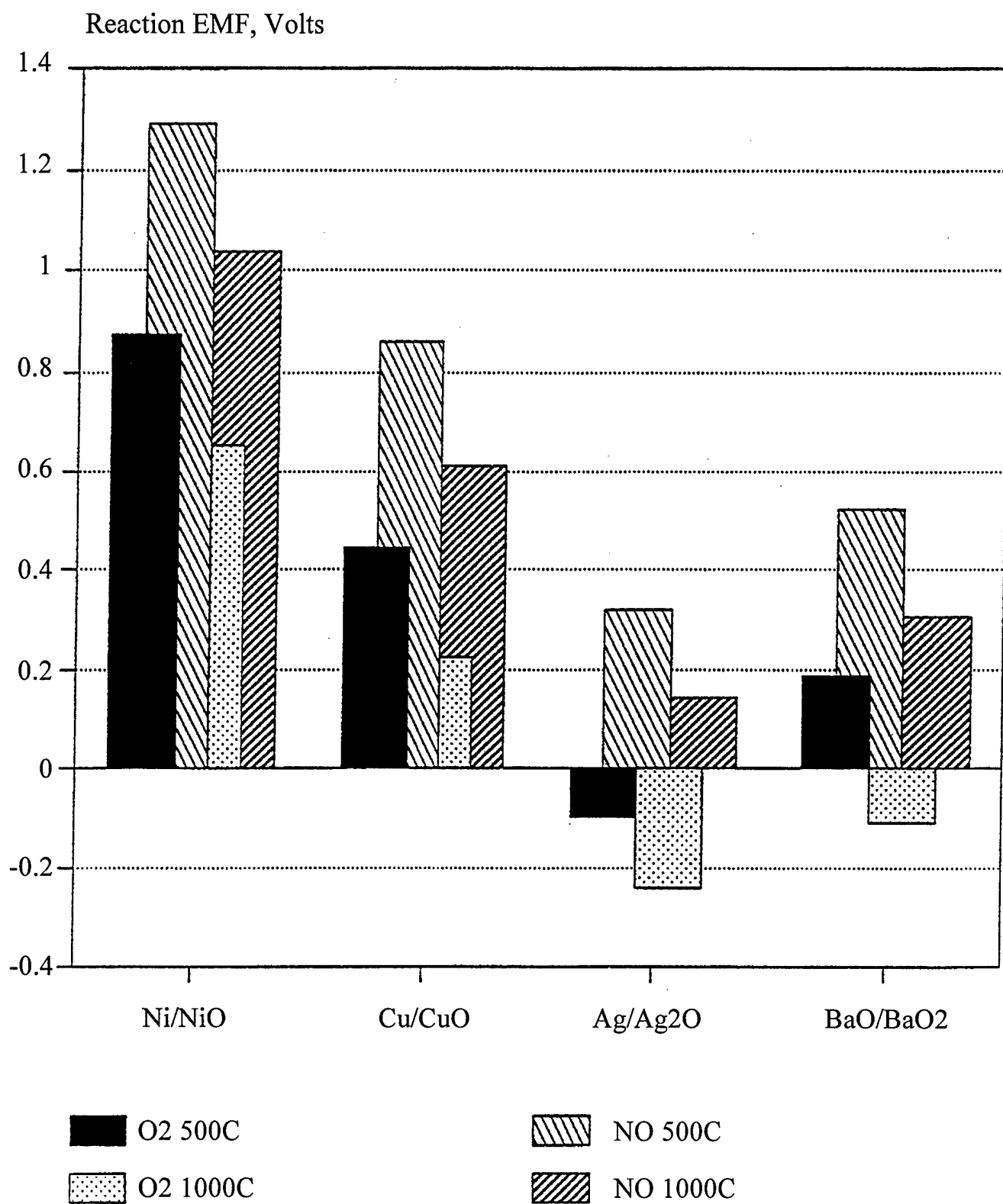


Figure 1, EMF For O₂ and NO

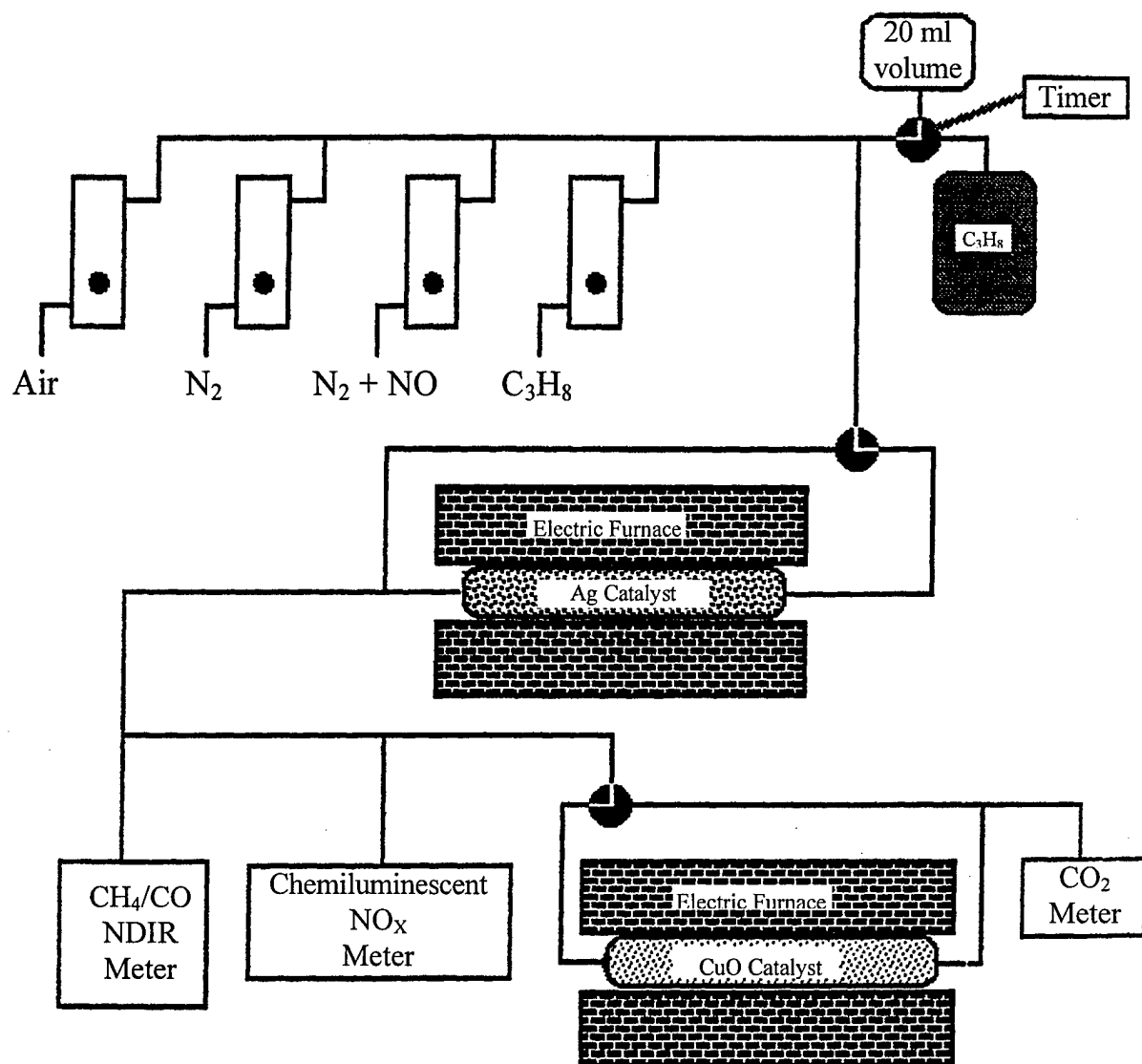


Figure 2
Experimental Setup for testing Reduction of NO_x with Ag on Alumine
with C_3H_8 in steady flow or in pulse flow

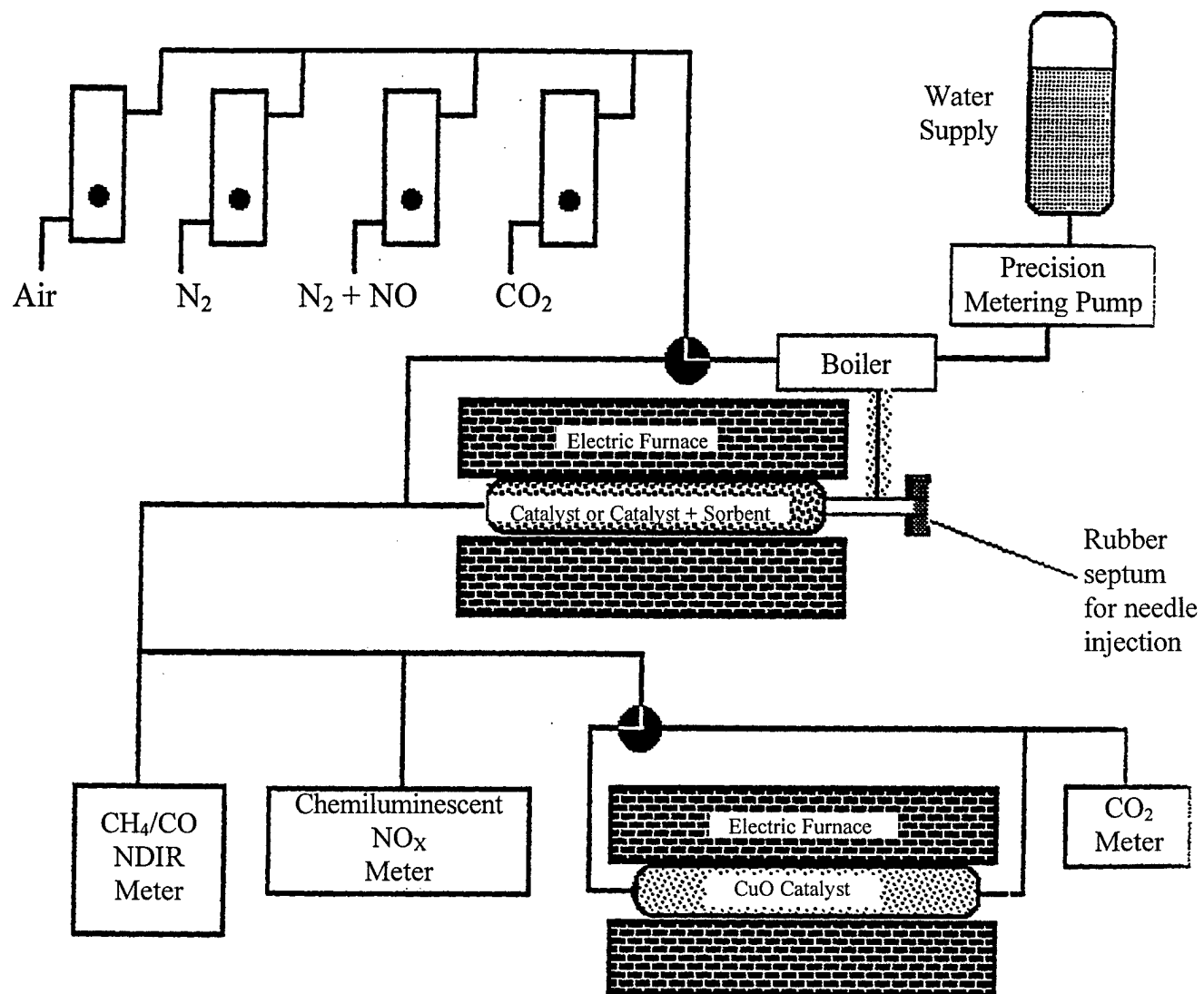


Figure 3
 Experimental Setup for Testing Reduction of NO_x
 with Ag on Alumine catalyst and/or a NO_x Sorbent and Combustion Catalyst
 by Pulsed Injection of Liquid Hydrocarbon

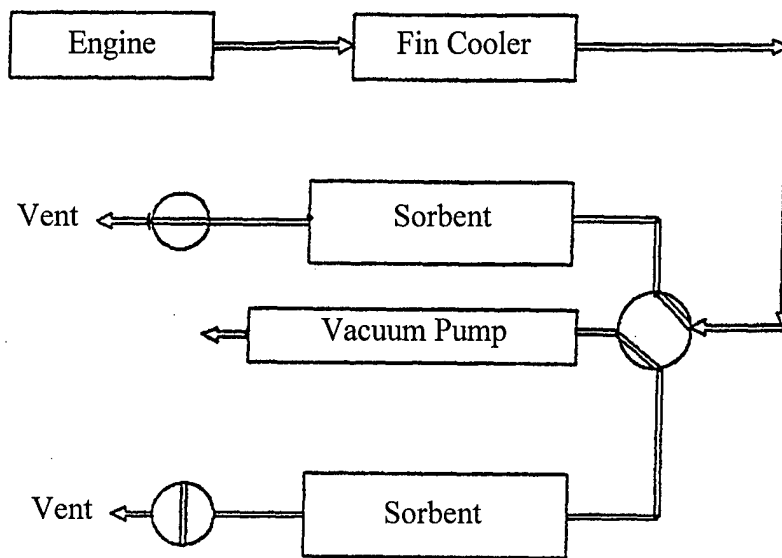


Figure 4. Conceptual Design: NO_x Control with a pressure-swing selective sorbent

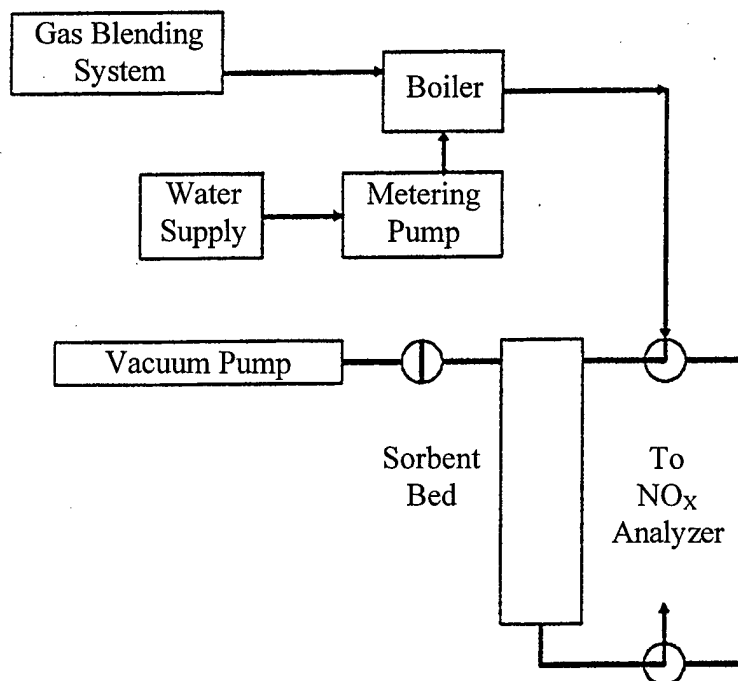


Figure 5. Experimental Setup for Sorbent Life Test

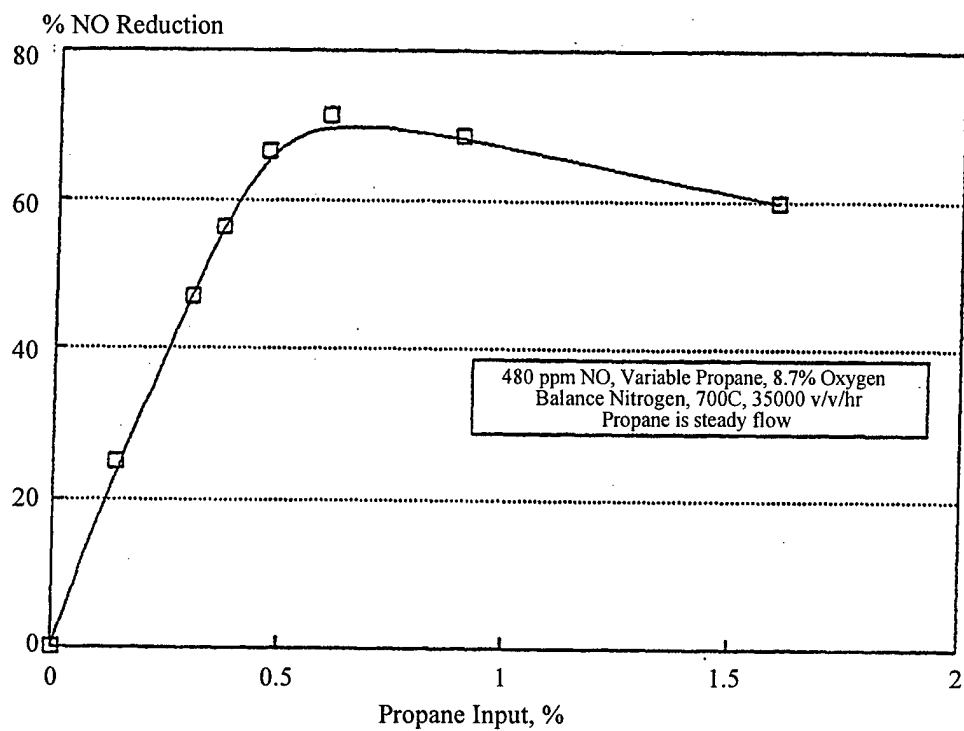


Figure 6, Reduction of NO on a 6.8 wt% Silver Catalyst

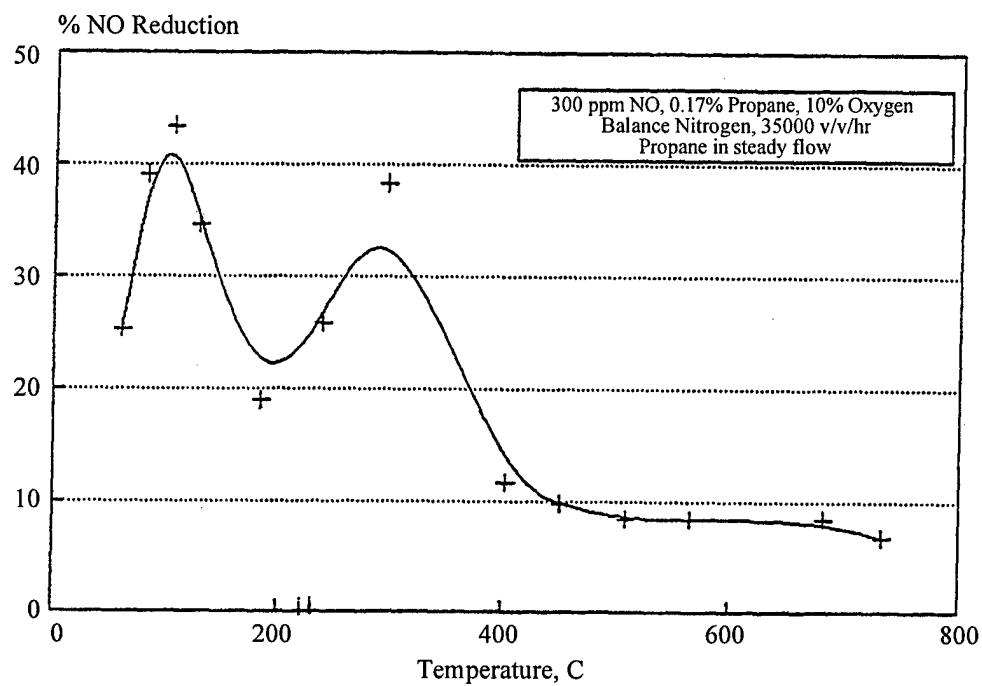


Figure 7, Reduction of NO on a 37.9 wt% Silver Catalyst

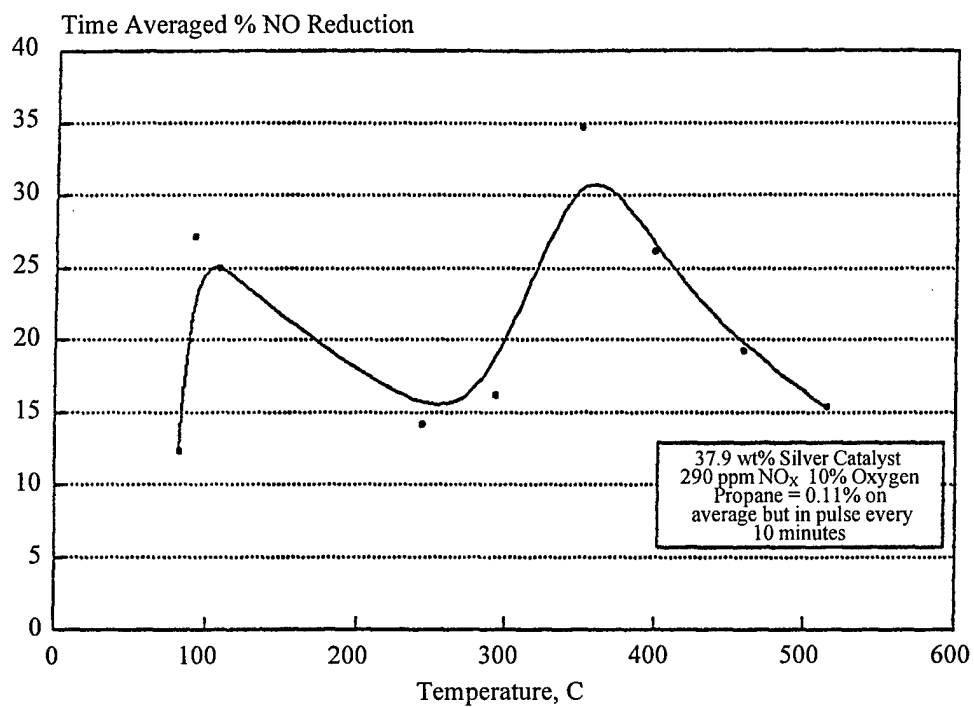


Figure 8, Reduction of NO with a Pulsed Flow of Propane

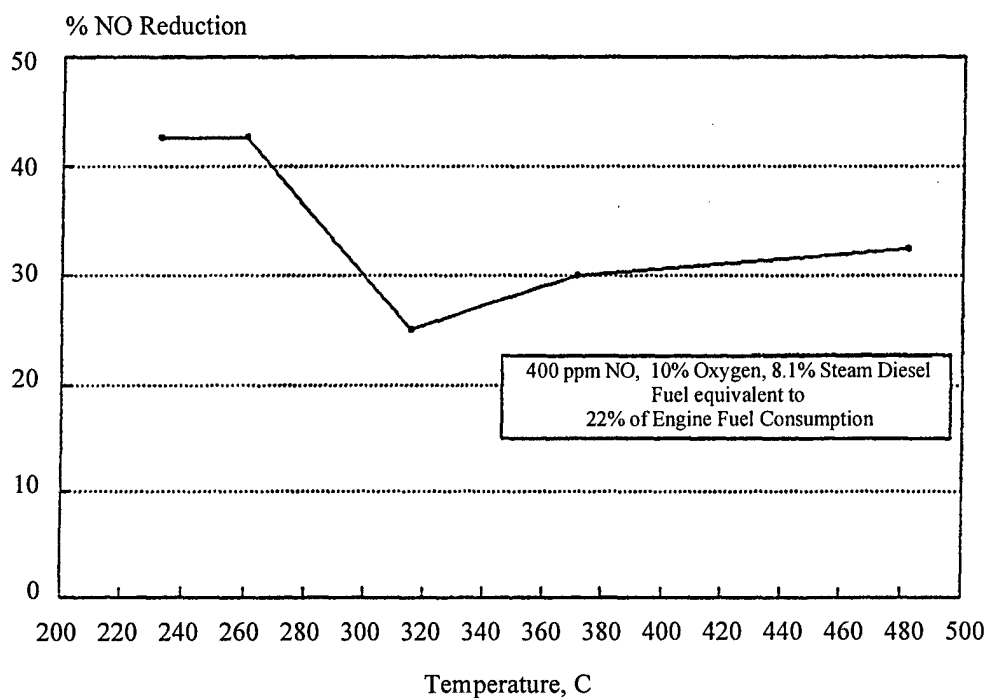


Figure 9, Reduction of NO with Diesel Fuel on a 37.9 wt% Silver Catalyst